

signal observed above the dark-current background, setting an atom ratio abundance limit $^{244}\text{Pu}/\text{Ir} \leq 1 \times 10^{-7}$. Thus, this line of evidence appears to discount a supernova event as the source of this Ir anomaly.

In summary, we have found a strong Ir abundance anomaly that coincides stratigraphically with the disappearance of several Cretaceous pollen species, which marks the K-T boundary throughout the western interior of North America. We believe that this is the first observation of the anomaly in conjunction with the palynological K-T boundary and in freshwater sediments. The $^{244}\text{Pu}/\text{Ir}$ atom ratio at the anomaly zone is $\leq 1 \times 10^{-7}$, about two orders of magnitude lower than would be expected from a supernova event.

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9. Preparation of the samples for ^{244}Pu mass spectrometric analysis was performed by L. Liepins. The mass spectrometric analysis was performed by R. E. Perrin.
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Tetramesityldisilene, a Stable Compound Containing a Silicon-Silicon Double Bond

Abstract. Irradiation of 2,2-bis(2,4,6-trimethylphenyl)hexamethyltrisilane in hydrocarbon solution produces tetramesityldisilene, which can be isolated as a yellow-orange solid stable to room temperature and above in the absence of air. Like the olefins of carbon chemistry, tetramesityldisilene undergoes addition reactions across the silicon-silicon double bond.

The diversity of organic chemistry arises in part because carbon readily forms multiple covalent bonds with other elements. The electronic structure of silicon is analogous to that of carbon, but the diversity of silicon chemistry has been limited by the lack of doubly bonded compounds, despite numerous attempts to synthesize them over the past six decades (1). Even compounds with a Si=C bond are rare, the first isolable one having been reported only this year (2). Evidence has been published for the transient existence of molecules with a Si=Si bond, analogous to the alkenes of

organic chemistry, but such disilene species have been postulated only as reaction intermediates (3, 4). They have also attracted the attention of theoreticians (5).

We report the isolation and characterization of tetramesityldisilene, a bright orange-yellow crystalline solid. In this compound, the Si=Si bond is sterically stabilized by the presence of two 2,4,6-trimethylphenyl (mesityl) groups bonded to each silicon. Tetramesityldisilene was synthesized by the photolysis of 2,2-bis(mesityl)hexamethyltrisilane in hydrocarbon solution (6) (Fig. 1). The best

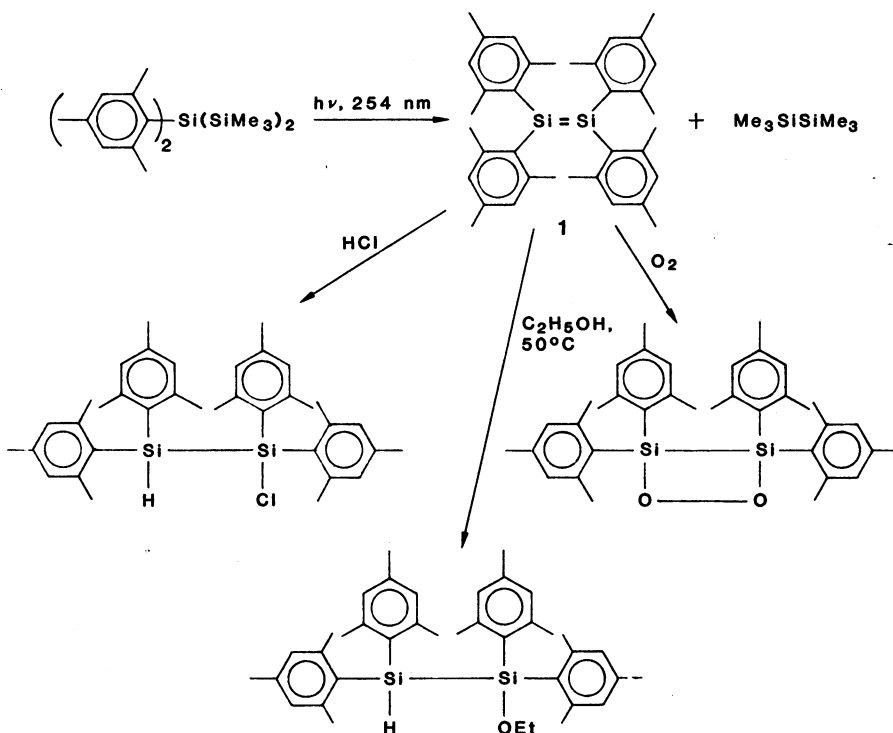
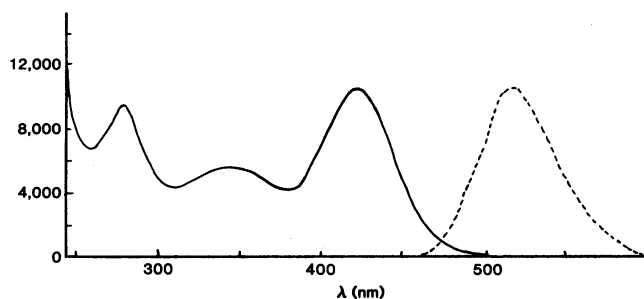


Fig. 1. Proposed scheme for the synthesis of tetramesityldisilene (1) and for the reaction of 1 with HCl, ethanol, and O₂; Me, methyl; Et, ethyl.

Fig. 2. Absorption (solid line) and fluorescence (dashed line) spectra of purified tetramesityldisilene (3-methylpentane, 77 K); ϵ is the molar extinction coefficient ($M^{-1} \text{ cm}^{-1}$). The absorption spectrum in hexane solution is identical.

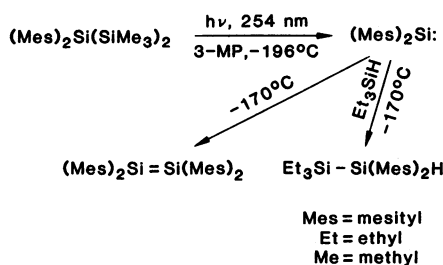


results were obtained when the photolysis was carried out in hexane or 3-methylpentane (3-MP) at -100°C (photochemical conversion about 80 percent). Under these conditions, the yield of tetramesityldisilene based on the amount of starting material photolyzed is ~ 95 percent. The product was purified by recrystallization from hexane. The physical and spectroscopic properties of tetramesityldisilene support the assigned structure (7).

Tetramesityldisilene is stable at room temperature in the absence of air, and in solution in hydrocarbons it is unchanged by brief heating to 160°C . The reactions of tetramesityldisilene are analogous to those of olefins in that this compound undergoes addition reactions across the double bond. For instance, it reacts rapidly with HCl to give the monochlorodisilane and with O_2 to yield 1,1,2,2-tetramesityl-1,2-disila-3,4-dioxetane. Ethanol adds slowly to the double bond to yield the ethoxydisilane (Fig. 1) (8).

The ultraviolet-visible absorption and fluorescence spectra of tetramesityldisilene are shown in Fig. 2. The strong absorption band at a wavelength (λ) of 420 nm, which we assign to the first $\pi \rightarrow \pi^*$ transition, is responsible for the yellow color of the compound. The large Stokes shift between the maxima of absorption and fluorescence (4000 cm^{-1}) indicates that the optical electron contributes significantly to Si=Si bonding, but the transition energy is much less than that found for analogous olefins; these results suggest that the Si=Si π bond is distinctly weaker than the C=C π bond.

The probable route of formation of tetramesityldisilene is by dimerization of the divalent silicon intermediate, dimesitylsilylene. Photolysis of the starting material in 3-MP at -196°C produces the blue silylene, isolated in the hydrocarbon matrix. The silylene may be trapped with a suitable reagent, for example, triethylsilane. If no trapping agent is present, dimerization to tetramesityldisilene takes place as the matrix is melted.



We have isolated a number of silylenes in 3-MP or argon matrices, including dimethyl- (9), diethyl-, and phenylmethyldisilylenes. When the matrix is slowly

and carefully warmed, all of these species undergo transformation into yellow intermediates with λ_{max} of 345, 345, and 420 nm, respectively. These also disappear with the formation of colorless polymeric products when the matrix is finally melted. We believe that the yellow intermediates are also disilenes and that in solution in the absence of trapping agents dimerization of silylenes to disilenes is general (10). Further polymerization takes place when the Si=Si bond is not protected by sterically bulky groups such as mesityl.

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7. The mass spectral data are as follows (the parenthetical number is the abundance relative to the tallest peak, taken to be 100): mass-to-charge ratio (m/e) 532 (37.4 percent), parent; 413 (26.6), parent ion-mesityl; 293 (33), (mesityl) $_2\text{Si-H}$; 265 (100), (mesityl) $_2\text{Si-H}$; 234 (42); 147 (31). Nuclear magnetic resonance (toluene solution, ^1H) δ values (parts per million): 2.05 (3H), $p\text{-CH}_3$; 2.43 (6H), $o\text{-CH}_3$; 6.67 (2H), Ar-H. Nuclear magnetic resonance (^{13}C) δ values: 21.2, 25.2, 128.6, 133.6, 138.9, 144.3. Nuclear magnetic resonance (^{29}Si) δ values: +63.6. The calculated composition (in percentages) for $\text{C}_{36}\text{H}_{44}\text{Si}_2$ is as follows: C, 81.12; H, 8.33; and Si, 10.55; the composition found was: C, 81.20; H, 8.42; and Si, 10.67. Molecular weight, isopiestic in hexane: calculated value, 532; value found, 530 ± 20 . Infrared spectrum, Nujol mull (in reciprocal centimeters): 1602 (s), 1029 (m), 847 (s), 722 (m), 631 (m), 598 (m), and 550 (m) (s = strong; m = medium). Raman neat crystal, Si=Si stretch at 529 cm^{-1} , strongly resonance-enhanced.
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10. Evidence for the dimerization of silylenes to disilenes in the gas phase has been presented by several groups (4).
11. This work was supported by the Air Force Office of Scientific Research (grant AF-AFOSR-78-3570) and the National Science Foundation (grant CHE-78-27094). We thank J. Radziszewski for assistance in determining the Raman spectrum.

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Airborne Lead and Other Elements Derived from Local Fires in the Himalayas

Abstract. *The combustion of wood and yak dung for heating and cooking in a populated Nepal Himalayan valley contributes significantly to the ambient airborne concentrations of lead, copper, aluminum, magnesium, and elemental and organic carbon. A comparison of the concentrations of these elements in fresh snow with corresponding values in air suggests that the pollution aerosol is confined to the valley, with pristine air aloft.*

Evidence of global transport of Pb and other elements in recent years has raised concerns about possible widespread human exposure to toxic species. Defining the natural concentrations is particularly important. Although typical concentrations of Pb in the blood of modern Americans are in the range of 15 to 25 μg per deciliter of blood, it has been estimated that concentrations were as low as 0.2 $\mu\text{g}/\text{dl}$ before use of the element had become widespread (1). Studies of human tissue as a more accurate indicator of long-term exposure than blood have also shown present-day elevations in Pb concentrations (2). It is thus possible that current American Pb body burdens often regarded as "normal" may actually be much greater than preindustrial concentrations and could be causing deleterious health effects (3).

The Pb concentrations in the bodies of people living in industrialized settings are probably linked to high overall concentrations in air, dust, water, and food. For example, typical airborne Pb concentrations in the United States are 30 to 450 ng/m^3 for rural areas and 500 to 2000 ng/m^3 for urban areas (4). Concentrations in the range from 0.05 to 0.2 ng/m^3 have been measured in the polar regions (5, 6), whereas preindustrial concentrations are thought to have been as low as 0.01 ng/m^3 (3). Our understanding of the relationships between environmental concentrations and exposure to Pb and other elements is far from complete, partly because of a lack of data on sources, transport pathways, and sinks, particularly in nonindustrialized areas.

The purpose of our study was to investigate sources of airborne Pb, Cu, Al,